# Preparation of nanosized barium zirconate powder by precipitation in aqueous solution.

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**Abstract**

Several ways were explored to synthesize barium zirconate by soft chemistry methods in aqueous solution. In the first method the synthesis of barium zirconate was initiated by urea decomposition, through an homogeneous precipitation of barium and zirconium salts followed by a "low temperature" thermal treatment. The kinetic of the reaction and the optimum urea/cation ratio have been determined by means of X-ray diffraction and Inductive Coupled Plasma analyses. It has been demonstrated that an amorphous zirconium hydrated oxide starts to precipitate followed by the precipitation of barium carbonate[1]. A calcination at 1200°C during 2 hours gives rise to the formation of a pure barium zirconate phase. In the other methods, barium zirconate was synthesized, in one step without any thermal treatments, by precipitation in highly basic aqueous solutions containing barium and zirconium salts. The effect of the hydroxide concentration was discussed in relation to the barium zirconate phase formation, the particles size and the particles size distribution. For each powder, microstructural characterisations have been performed on sintered bodies in order to evaluate the influence of the thermal treatment on the final density. Dilatometric measurements have been also performed in order to quantify the densification process. Important informations were obtained by these techniques, as for example the existence of an internal porosity which severely limits the final density of the material, even if sintering was performed at high temperature. Thus a careful control of the heating profile seems to be necessary in order to produce dense materials.

## 1.Preparation of nanosized barium zirconate powder by thermal decomposition of urea in aqueous solution containing barium and zirconium, and calcination of the precipitate.

It is well know that the pH of a salt solution can be increased homogeneously by using the thermal decomposition of urea at about 90°C. The decomposition of urea gives rise to a controlled release of ammonia and carbon dioxide into the solution. $OH^-$ and $CO_3^{2-}$ ions induce the precipitation of metal hydroxides and/or hydroxycarbonates [2] which are the precursors for the perovskite compounds.

In order to produce a precursor with a barium/zirconium ratio equal to 1 from solutions containing barium and zirconium chloride, ICP measures were performed on the solid phase for different molar ratios urea/cations and different decomposition time.

Quantitative precipitation is observed for a urea/cations molar ratio equals to 30 and a decomposition time of 24 hours.

The precursor is a mixture of crystalline barium carbonate and an amorphous hydrated zirconia phase. This reactive mixture was calcined to produce barium zirconate and the phase evolution was followed as a function of the temperature by XRD measurements as shown on figure 1. Pure barium zirconate phase is formed at about 1100°C . The particles are spherical and their size lies in the

range of 50 to 120 nm with some bigger aggregates characterized by a diameter close to 300 nm. A lot of neck-formation between particles can be seen on figure 2.

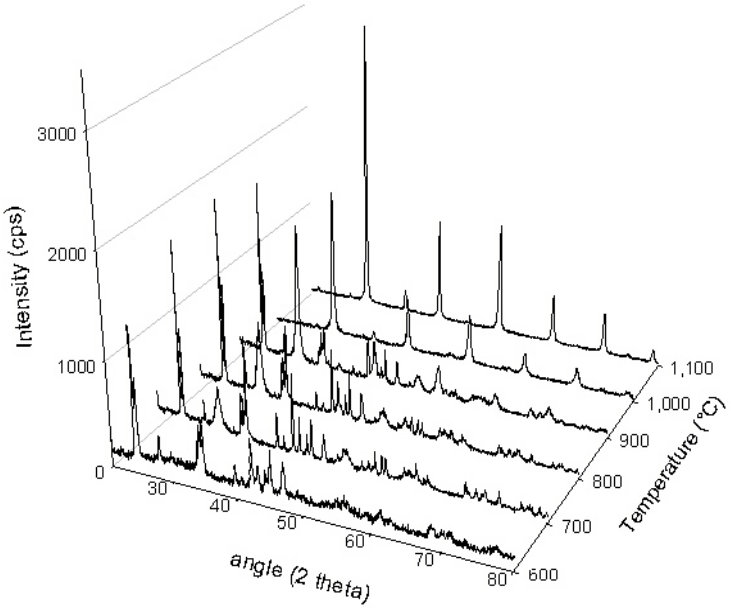


Figure 1: Evolution of the reacting mixture calcined between 600°C and 1100°C

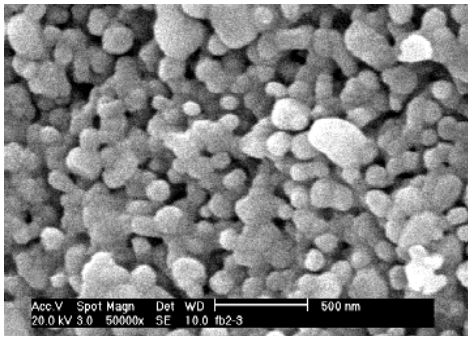


Figure 2: photomicrographs of calcined $BaZrO_3$ powder at 1200°C for 2 hours. Magnification rate 50000X.

**Sintering of the powder.**

As shown by the dilatometric studies, the onset of shrinkage starts between 1250 and 1300°C. SEM photomicrographs of the pellets surface sintered at 1200°C (A), 1300°C (B), 1400°C (C) and 1500°C (D), for 2 hours with a heating rate of 3°C/min (figure 3) were taken to study the temperature effect on the densification of the material. Shrinkage at 1300 °C are confirmed by the photomicrographs. No open porosity can be observed after a sintering temperature at 1500°C for 2 hours. Although, Archimede's measurements on the pellets indicated an important open porosity equal to 26 % at 1200°C which decreases to 3.6 % by rising the sintering temperature at 1500°C (Figure 4). Moreover, $BaZrO_3$ sintered at 1400 and 1500°C shows a strong enlargement in grain size (figures 3).

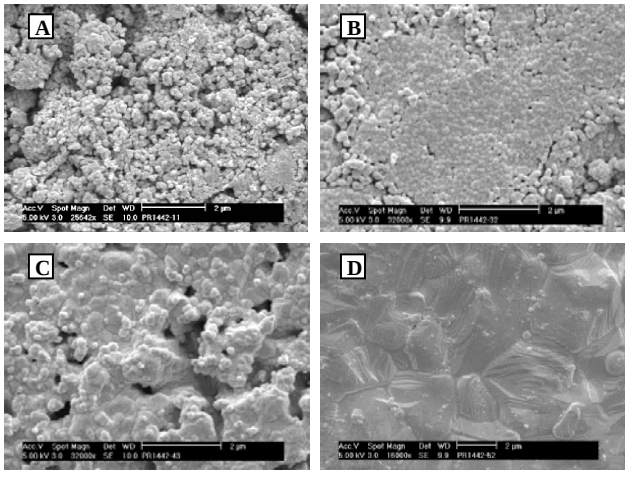


Figure 3: SEM photomicrographs of the pellets surface sintered at 1200°C (A),1300°C (B), 1400°C (C) and 1500°C (D), for 2 hours.

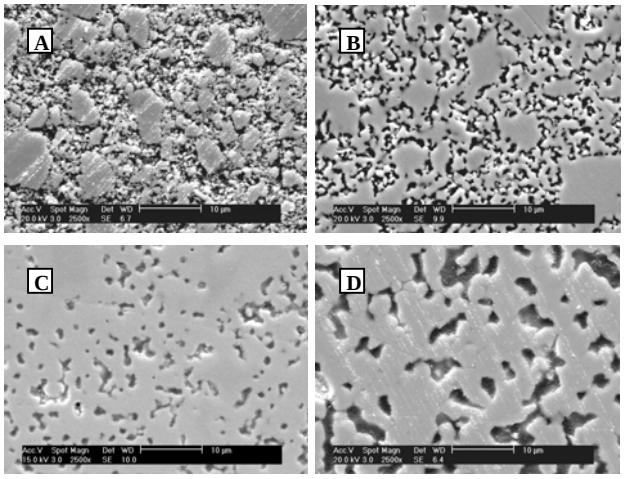


Figure 4: SEM photomicrographs of polished cross section of $BaZrO_3$ pellets sintered at 1200°C (A), 1300°C (B), 1400°C (C), and 1500°C(D) for 2 hours. Magnification rate 2500X.

The average grain size is in the range of 150 nm around 1300°C, 400 nm around 1400°C and 3 µm around 1500°C. Thus, the enlargement in grain size is believed to contribute to the decrease of the sintered density. SEM photomicrographs of polished cross section of $BaZrO_3$ pellets sintered at 1200°C (A), 1300°C (B), 1400°C (C), and 1500°C(D) for 2 hours with a heating rate of 3°C/min show some internal porosity. That residual porosity can probably be explained also by the decomposition of some residual barium carbonate. The final density of the pellet sintered at 1500°C is about 93.3%.

**2. Synthesis of barium zirconate by homogeneous precipitation in highly basic aqueous solutions.**

The aqueous solution containing an equal ratio of barium and zirconium chloride (0.25M) was added at a constant flow into a stirred 15 molar NaOH solution preheated at 80°C. The reaction time was set to 15 minutes. The precipitate was then isolated by centrifugation at 4000 rpm and washed with water before drying.

The influence, on the barium zirconate formation, of the sodium hydroxide concentration (7.5,10,12.5,15M), flow rate, reaction time and total concentration of the reactants was studied in order to optimise this synthesis.
We observed a striking influence of the hydroxide concentration on the purity and the crystallinity of the precipitated powder. When the concentration of sodium hydroxide is higher or equal than 12.5 molar, pure spherical crystalline barium zirconate particles with a barium/zirconium ratio equal to 1 can be directly obtained without any other heating treatment (figure 5). Particle size depends on the total concentration of reactant. Spherical particles with a diameter around 0.5 µm can be produced by adding a 0.25 molar stock cations solution to a 15 molar sodium hydroxide solution.

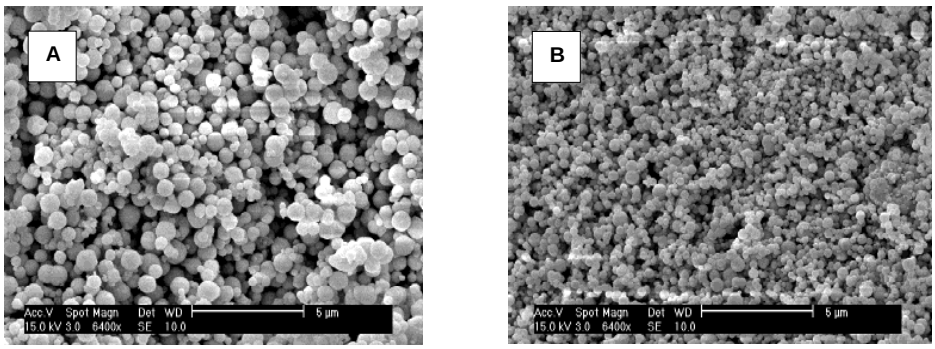


Figure 5: pure barium zirconate particles obtained by adding a total concentration of reactant equal to 0.25 molar (A) and 1 molar (B)

For sodium hydroxide concentration less than 12.5 mol/l, ATG analysis confirms a loss of mass after 900°C which can be assigned to some barium carbonate decomposition (figure 6). The presence of carbonate phase is confirmed by the FTIR spectra (figure 7). In other hand, no characteristic bands of carbonate can be observed for powders precipitated in solution with sodium hydroxide concentration equal to 15 mol/l. Even if a small mass loss is observed at 900°C for powders synthesized with a sodium hydroxide concentration up to 12.5 mol/l, it seems that high sodium hydroxide concentration prevents carbonation of the synthesized powders despite of the fact that the reaction is performed in air. Thus, in a highly concentrated sodium hydroxide solution, the

chemical equilibrium is shifted to the formation of pure $BaZrO_3$ phase with no carbonate phase contamination.

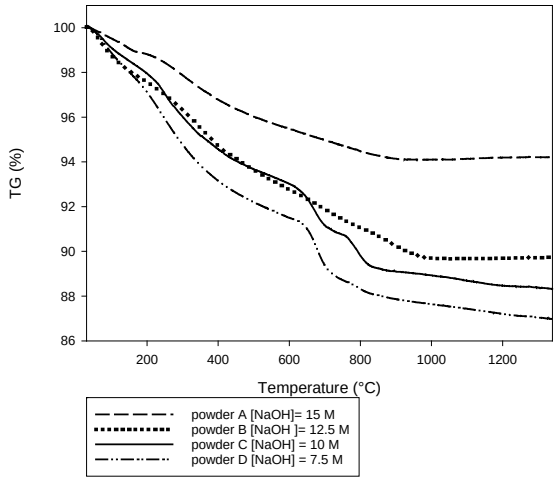


Figure 6: TG curves of powders obtained at different sodium hydroxide concentrations.

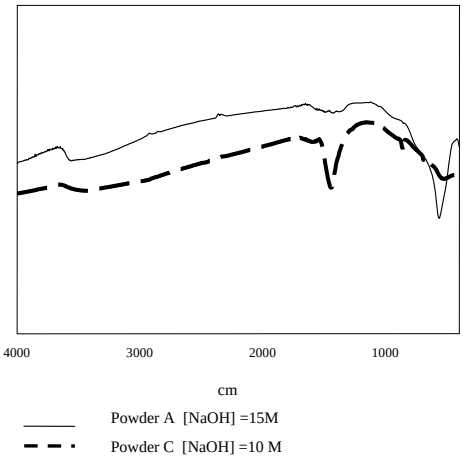


Figure 7: FTIR spectra of powders obtained at sodium hydroxide concentration of (A) 15M and (B) 10M

## Sintering

The morphology of the surface of a pellet prepared with a powder obtained by precipitation in highly concentrated sodium hydroxide solution is shown in figure 8.
This pellets was sintered at 1650°C for 12 hours.
Its density was 95.6% of the theoretical density.
No open porosity can be observed and median grain size is 2.6 µm.

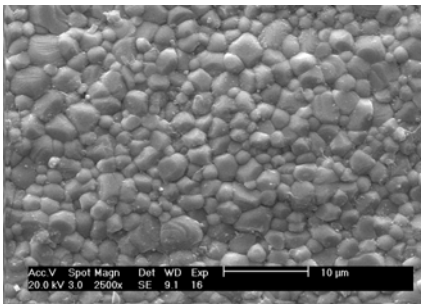

Figure 8:surface morphology of a pellet sintered at 1650°C for 12 hours. Magnification

## Conclusion

We showed that synthesis of powders by aqueous thermal decomposition of urea is very simple to use, and can give very small particles with typical grain size around 90 nm. Only two hours are necessary to obtain pure $BaZrO_3$. But by that method, it is not possible to avoid the carbonate formation. The final density of the pellet is 93.3 % of the theoretical one after a sintering at 1500°C during two hours.
On the contrary, in highly basic solution, pure fine crystalline $BaZrO_3$ powder can be produced in one step in 15 minutes by a simple precipitation process. The high basicity of the solution prevents the formation of barium carbonate phase and allows the formation of a well crystallized $BaZrO_3$ perovskite phase. This process is very fast and can be designed to recycle the reactants.
But progress have yet to be done in order to increase the density of the end-product and to resolved the problem of the trapped porosity observed by the two methods.

## References

[1] T.Gangadevi, M. Subba Rao and T.R. Narayanan Kutty, J. Thermal. Anal. 19 312-332 (1980).

[2] B.C. Cornilsen and J.S. Reed, Am. Ceram. Soc. Bull., 58, 1199-2000 (1979).